

CHARACTERIZATION OF VISCOSE FORMULATIONS THROUGH RHEOLOGICAL AND PHYSICOCHEMICAL PARAMETERS

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ABSTRACT

The characterization of processing viscose solutions through their shear viscosity function is presented to infer relevant microstructural properties of cellulose chains in the formulated aqueous solvent. Thus correlations between simple rheological models and classical physicochemical parameters are analyzed and discussed. Three viscose samples were prepared from eucalyptus dissolving pulp treated with and without mechanical-enzymatic process to obtain different degrees of polymerization (DP) and reactivity of cellulose chains. The effect of this combined pulp pre-treatment on viscose shear viscosity function is quantified experimentally through the gravity-driven capillary viscometer. Since viscose solutions presented a rather constant viscosity around the overlap concentration at high shear rates, the shear viscosity was studied mainly at relatively low values of shear rate to visualize a subtle plastic response. Within an analysis of simple models concerning the behavior of shear thinning fluids, rheological parameters of the Bingham model, like plastic viscosity and yield shear stress, were determined for the three viscose solutions. These results are analyzed in relation to relevant physicochemical properties typically used in most cellulose technological applications like chain solubility in alkali, Fock reactivity, intrinsic viscosity and DP of both original and treated pulps. Further the quality of viscose was established through the determination of cellulose and total alkali contents, degree of substitution (DS) and salt index (SI). Finally regenerated cellulose films were obtained through an acid bath to determine their intrinsic viscosity and DP. Results showed that cellulose chains presented a complex conformational shape, where effective electrical charge and hydration were the controlling parameters.

KEYWORDS: Cellulose dissolving pulps, Gravitational capillary viscometer, Shear viscosity, Viscose formulations.

INTRODUCTION

Cellulose is an important biopolymer with valuable properties like biocompatibility, biodegradability and chemical and thermal stability. The growing interest of this renewable natural source, with high economical impact in new products for science, technology and medicine and modern materials, generated a revival of multidisciplinary cellulose researches [1].

The main disadvantage in cellulose processing is its insolubility in most common solvents. This unfavorable property is a consequence of cellulose high crystallinity stabilized through strong inter- and intra-molecular hydrogen bonds, impeding the effective solvent imbibitions of this structural phase [2]. To overcome this difficulty, cellulose may be modified by derivatization reactions which greatly expand the applications of this natural resource. At present the manufacture of both cellulose derivatives and regenerated cellulose products have still many relevant applications via viscose solution formulations, despite new technological trends contemplate innovations for cellulose dissolution to exploit better the biocompatibility of this natural polymer [3].

For the purposes of the present work, it is relevant to visualize that the solvent accessibility within the cellulose fibers is limited by the compact structure of cellulose, which is determined by the presence of highly ordered regions [4]. Therefore, a challenge in the production of regenerated cellulose is to achieve the complete dissolution of the cellulose structure to obtain homogeneous products. In this regard there is consensus establishing that the solvent access into cellulose depends mainly on the number and size of pores in the cellulose structure. Therefore, native pores, fibril aggregates and highly ordered regions must be substantially modified to increase cellulose structural openness [5].

In particular, to overcome the cellulose solubility problem and still within the framework of the classical processing via viscose solutions, in recent years several studies have proposed the use of chemical, mechanical or enzymatic pre-treatments, and combination of them, to increase cellulose accessibility and reactivity [5-7]. Thus when the pulp is subjected to mechanical treatment, the inter-fibril bonds, mainly located in the outer wall of the cell are disrupted. This operation provokes an increase in the reactive surface area of fibers, improving the accessibility of cellulose [5]. Further enzymatic treatment is used to modify the degree of polymerization (DP) and chain reactivity with non-toxic byproducts and an environmentally harmless process. In this regard, cellulases acting on dissolving pulps offer a great potential for pre-treated cellulose pulp [8-10].

It is worth to observe that regenerated products involving fibers, films, membranes and sponges, among many others, constitute a large production sector of cellulose derivatives. For these purposes, the industrial viscose process is one of the most used with an annual worldwide production of 3.5 million tons [11]. In this process the dissolving pulp is treated with carbon disulfide to obtain a metastable intermediate cellulose xanthate, which is then dissolved in dilute aqueous NaOH to form the viscose solution. Molded products are obtained when the processed and well shaped viscose solution is chemically or thermally treated to yield regenerated high purity cellulose.

It is also relevant to indicate here that cellulose derivatives are obtained from special dissolving pulps [7]. These pulps generally have high cellulose content (90-98%), low hemicelluloses, extractives and minerals contents, high brightness, quite uniform molecular weight distribution, and a high DP. Therefore they usually require an aging step to reduce the DP to an optimal working level.

Another relevant parameter determining the physical and chemical properties of cellulose derivatives is the degree of substitution (DS) [12], which for viscose is defined as the number of xanthate groups per anhydroglucose unit of the cellulose.

Finally viscose ripening may be necessary to obtain a good performance in the spinning process achieving appropriate properties of the final regenerated products. In this regard, chemical and physical changes occur in viscose during ripening. Thus the viscose solution viscosity first evolves decreasing because the microstructure becomes more uniform in relation to the distribution of xanthate groups along the chains. Then this viscosity starts to increase with a faster rate as xanthate groups decompose allowing the formation of a gel network. The degree of ripening is controlled through process time and thermal history thus defining the optimal processing viscosity. One empirical parameter providing the viscose ripeness is usually the salt index (SI) which is the sodium chloride solution concentration required to coagulate the viscose [13] in a prefixed volume.

Within the above technological description the present work places emphasis on the use of rheological parameters to characterize viscose solutions in correlation with those classical physicochemical parameters typically used in the cellulose industry.

MATERIALS AND METHODS

Raw material and pulp pre-treatment

Here we used eucalyptus dissolving pulp Solucell[®], which was a pre-hydrolyzed kraft pulp bleached through a totally chlorine free sequence. The diminution of the degree of polymerization and increase of reactivity of the original pulp previous to the preparation of viscose was carried out through a combined mechanical-enzymatic pre-treatment. The mechanical effect was introduced through a laboratory PFI mill at 6000 revolutions. Then a treatment with the enzyme Maximyze 2530 was applied to the refined pulp. This hydrolysis was carried out with a dosage of 9 % at 45 °C in NaH₂PO₄/Na₂HPO₄ buffer of pH 7 and pulp consistency of 5 % w/w. The reaction time was 3 hours in a stainless steel batch reactor equipped with double sigma helices mixing system and jacket for temperature regulation. Then the enzyme was deactivated in boiling water for 10 minutes and the pre-treated pulp was finally washed and stored at low temperature.

Pulp physicochemical parameters

The original and pre-treated pulps were characterized through several analytical techniques with the aim to test the effect of mechanical refining and enzymatic hydrolysis. Thus alpha-, beta- and gamma-cellulose (TAPPI T203 cm-99) and alkali solubility in NaOH (9 % w/w) at -5 °C [14] were determined. Also Fock reactivity [15], intrinsic viscosity [η]_o in cupriethylenediamine and viscometric DP were evaluated [16].

Viscose preparation

The viscose solutions were prepared by following a previous work [17]. Thus pulp was immersed into NaOH to obtain alkali cellulose (AC) which underwent an aging step to control and reduce the DP. Then the aged AC reacted with CS₂, which was added in a concentration of 25 % determined according to the amount of cellulose in the AC. Finally the solid cellulose xanthate was dissolved in NaOH to form the final viscose solution.

Through this process, three viscose solutions were prepared with the following codes and characteristics: V1 was obtained from the original pulp through the basic process with an accelerated ripening step at around 30 °C; V2 was obtained from original pulp through the basic process, and hence it was considered the reference viscose sample for discussions below; V3 was prepared by including a mechanical-enzymatic pre-treatment of the original pulp. Figure 1 illustrates the basic process steps involved here.

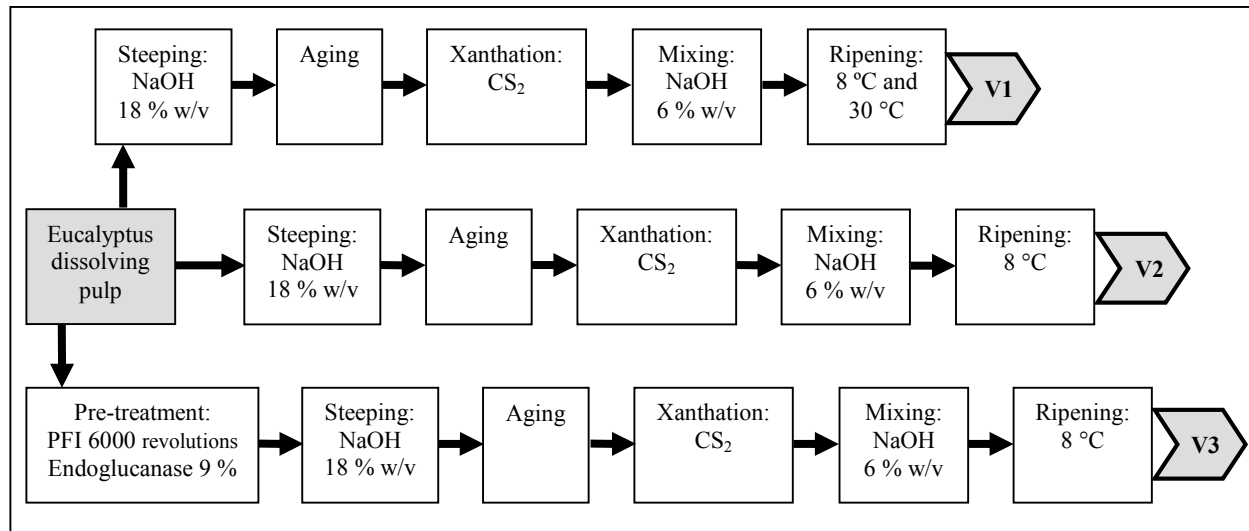


Figure 1. Schematic viscose processes for V1, V2 and V3.

It must be pointed out that the preparation processes of V2 and V3 had a ripening step of seven days at

around 8 °C, while this step for V1 considered two parts, one was at 8 °C during five days and the other was at 30 °C for two days, thus introducing a more effective ripening.

Viscose physicochemical parameters

The quality of the viscose solutions obtained was evaluated through conventional analytical techniques to determine SI and contents of cellulose, total alkali [18] and carbon disulfide as xanthate to calculate the DS [19].

Also regenerated cellulose films were obtained from the viscose samples with H₂SO₄ (10 % w/v) containing anhydrous MgSO₄ in a concentration 2 % w/v. Therefore the intrinsic viscosity and DP [16] were determined from these films as additional characterization parameters of the viscose performances.

Gravitational capillary viscometry

Two gravitational capillary viscometers were built [20, 21] in our laboratory. Therefore Viscometer 1 had a capillary radius R=0.2527 cm and a length L=10.1 cm, while Viscometer 2 had R=0.1171 cm and L=9.5 cm. The viscometric tests were performed at 20 °C. The three viscose samples were studied in the Viscometer 1. The reference viscose V2 was also measured in the Viscometer 2 to visualize the change of shear rate range due to a decrease of the capillary radius size, and also to observe flow end effects.

THEORETICAL ASPECTS

Intrinsic viscosity

The solution specific viscosity is calculated from $\eta_{sp} = (\eta - \eta_o) / \eta_o$ where $(\eta - \eta_o)$ is the difference between polymer solution and pure solvent viscosities, respectively. Measurements are carried out through an Ubbelohde capillary viscometer (IVA). Since the polymer concentration C in the solutions used for this test must be within the very dilute range, $\eta_{sp} \approx (t - t_o) / t_o$ is satisfied, where t and t_o are the draining times measured for sample and solvent, respectively. It is clear that the intrinsic viscosity $[\eta]_o$ is a measure of the increase of solvent viscosity due to the presence of the polymer in the absence of intermolecular chain forces because $[\eta]_o = \lim(\eta_{sp} / C)$ for $C \rightarrow 0$. To obtain this asymptotic value the semi-empirical equation of Schulz-Blaschke is used $[\eta]_o = (\eta_{sp} / C) / (1 + K_\eta \eta_{sp})$ where $K_\eta = 0.29$ for cupriethylenediamine [22, 23].

In this framework the degree of polymerization is obtained from the Staudinger-Marx-Howink equation, $[\eta]_o = K_{DP} DP^a$ (1)

where K_{DP} and a are constants depending on the solvent-polymer pair interactions and the range of polymerization. They satisfy $K_{DP} = 0.42$ and $a = 1.0$ for $DP < 950$ while $K_{DP} = 2.29$ and $a = 0.76$ for $DP > 950$ [23].

Shear dependent viscosity models

At present it is known that at least four parameters are required to predict the generic form of the shear viscosity $\eta = \tau / \dot{\gamma}$ as a function of the shear rate $\dot{\gamma}$ in fluids showing shear thinning response [24]. Here τ is the shear stress of the fluid. For instance the Cross equation has the following expression $(\eta_o - \eta) / (\eta - \eta_\infty) = (K\dot{\gamma})^m$ where η_o and η_∞ are the zero and infinite shear rate viscosities, respectively, and K is a characteristic relaxation time in the semi-dilute solution regime. For the particular case where $\eta \ll \eta_o$, the Sisko model is obtained with $m = 1 - n$. For $n = 0$ the result is the

Bingham model as follows

$$\eta = \eta_p + \tau_y / \dot{\gamma} \quad (2)$$

where $\eta_p = \eta_\infty$ is the plastic viscosity and $\tau_y = \eta_o / K$ is the yield shear stress. When the resulting shear viscosity has an extreme pseudoplastic behavior, one infers the existence of a discrete microstructure of the "suspension type" which is different from that found in most macromolecular solutions in this concentration range. Generally it is required to investigate this model at low values of $\dot{\gamma}$ in order to qualitatively describe the ideal change from $\tau < \tau_y$ (no flow) to $\tau > \tau_y$ (flow).

RESULTS AND DISCUSSION

Table 1 shows that the original pulp used here meets the requirements of a "high purity pulp" to be used in viscose preparations [7]. It has a high content of α -cellulose (around 95 %) and low content of hemicelluloses (visualized through the 0.99 % of γ -cellulose). These compositions are reduced after the mechanical-enzymatic pre-treatment. Thus a decrease of around 6 % and 22 % for α -cellulose and γ -cellulose are accompanied with an increase of around 156 % of β -cellulose.

To visualize even better the effect of the enzymatic pre-treatment, it is important to point out that the enzyme used here is the endoglucanase Maximize 2530. This type of enzyme cleaves amorphous sites of cellulose creating shorter chains [25]. Therefore it is expected the decrease of α -cellulose as a consequence of the increase of the content of degraded β -cellulose as shown in Table 1.

Table 1. Pulp physicochemical parameters.

Dissolving pulp	α -cellulose (%)	β -cellulose (%)	γ -cellulose (%)	Solubility (%)	Fock reactivity (%)	$[\eta]_o$ (ml g ⁻¹)	DP
Original	95.25	3.76	0.99	34.2	68.4	428	993
Pre-treated ^(a)	89.62	9.61	0.77	78.5	88.8	275	656

(a) - Mechanical-enzymatic processing.

In addition the intrinsic viscosity and hence de DP of the pulp were reduced to 275 ml/g and 656, respectively. In fact the decrease in DP was within acceptable levels to obtain good quality of cellulose derivatives. For example, to form rayon of high toughness, the pulp intrinsic viscosity needs to be lowered to 200-300 ml/g for the viscose spinning process [9].

It is also clear that the pulp mechanical pre-treatment leads to an increase in the reactive surface area of the fibres, improving the solvent accessibility of cellulose [5]. In these conditions, the enzyme is able to interact with the amorphous regions of cellulose producing their effective hydrolysis so that the polymeric matrix becomes more open and accessible to chemical reactions. In this context, the alkaline solubility in NaOH (9 % w/w) at -5 °C was increased from 34 % to 78 % and the Fock reactivity was also higher as shown in Table 1.

The physicochemical parameters of the three viscose samples are shown in Table 2. From these results one finds that V1 has a higher content of cellulose than V2 and V3, although they are similar regarding their contents of total alkali. The values of DS and SI of V1 differ from those of reference V2. Both viscose samples were made from the same original pulp but the first one was ripened for 48 hours at 30 °C

(see Fig. 1). In this step the viscose undergoes a maturation process in which the substitution becomes more uniform and xanthation continues the generation of more byproducts and hence the DS decreases [13]. Thus for V1 the reduction of the DS and SI values in relation to those of V2 are expected as shown in Table 2. On the other hand, V3 made from the mechanical-enzymatic pre-treated pulp shows a relative lower degree of substitution than that of the reference V2, probably due to different chemical characteristics between pulps (Table 1).

Table 2. Viscose physicochemical parameters.

Viscose	Cellulose (%)	Alkali (%)	CS ₂ ^(a) (%)	DS	SI (%)
V1	5.9	7.5	0.99	0.36	3
V2	5.1	7.4	1.18	0.50	10
V3	5.0	7.7	0.86	0.37	(b)

(a) - Carbon disulfide as xanthate. (b) - No available.

Figure 2 shows η as a function of $\dot{\gamma}$ for the three viscose samples studied here through Viscometer 1. During the ripening step, chemical and physical changes take place in the viscose. The viscosity of the solution increases as the cellulose xanthate decomposes (lower DS and SI) and eventually forms gels prior to regenerate into cellulose again [13]. Consequently it was expected that the sample V1 ripened presented higher shear viscosity than that of V2, as shown in Fig. 2. Table 3 shows the fitting of experimental data with Eq. (2) to obtain rheological parameters η_p and τ_y in relation to viscose intrinsic viscosity and DP. The fits of rheometric experimental data generated a correlation coefficients $r^2 > 0.999$, indicating that for low values of $\dot{\gamma}$ the viscoses studied here satisfied well the Bingham model (the asymptote η_p is achieved for $\dot{\gamma} > 100 \text{ s}^{-1}$) showing consistency between model and experiments. On the other hand, others well known pseudoplastic models for the fitting procedure were found physically inappropriate.

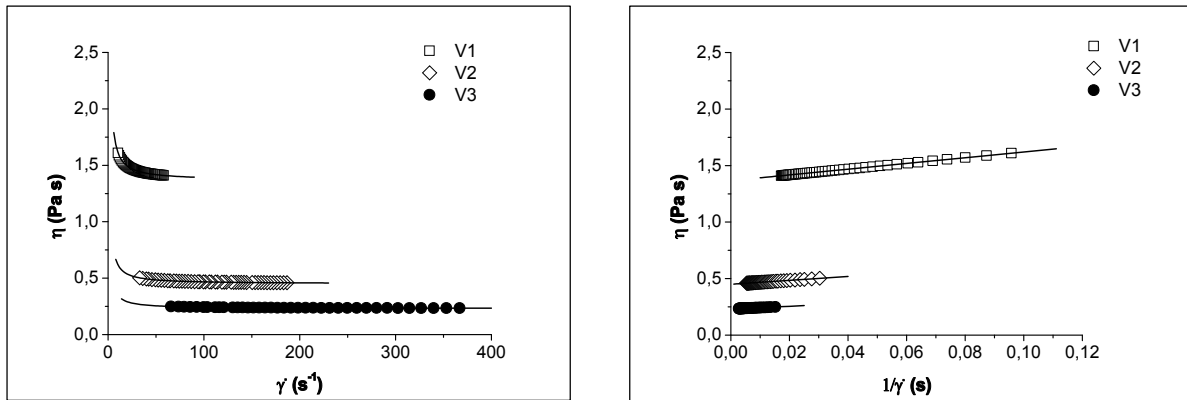


Figure 2. Shear viscosity as a function of shear rate. Solid lines are fits of experimental data (symbols) with the Bingham model.

To visualize the correlation between these preliminary results, one observes from Fig 2 that η_p increased consistently with DP (Table 3). Moreover, the plastic viscosity increased when DS diminished due to

thermal decomposition of xanthate groups in the ripening step yielding less chain electrostatic repulsion with more network formation. It was found that the Bingham model represented well solutions for the semi-dilute concentration regime with $C^* < C$, where C^* is the polymer overlap concentration. Here $C^* \approx 0.004 \text{ g/cm}^3$ as estimated from $C^* \approx M / R_g^3 N_A$, where M is the polymer molecular mass evaluated by considering DP and DS values, N_A is the Avogadro constant, R_g is the radius of gyration defined $R_g \approx L \sqrt{C_N} \sqrt{DP}$ where L is the length of the monomer unit in the chain, and C_N is associated with the chain flexibility. For synthetic polymers the asymptotic value $C_N \approx 9$ applies while for polyelectrolyte chain this value may be either higher.

Table 3. Evaluation of viscose rheological parameters.

Viscose	$[\eta]_o^{(a)}$ (ml g ⁻¹)	DP ^(a)	η_p (Pa s)	τ_y (Pa)
V1	221	527	1.367	2.539
V2	201	478	0.450	1.737
V3	167	398	0.231	1.204

(a) - Values of the regenerated cellulose films obtained from viscose.

Results also suggest that the dissolution of cellulose chain obtained may have a relatively open and highly hydrated structure due to negative groups $-S^-$ formed. By using DS values obtained, we estimated that the negative charge number per chain varies from -147 to -239 generating for the three viscose samples a high electrostatic repulsion among hydrated particles. These results suggest the need of using rheological models constructed from the consideration of electrokinetic phenomena of the solution microstructure as a relevant physicochemical aspect associated with different viscose formulations. Further, it is clear that viscose solutions require to be characterized rheologically before they can be appropriately used in different types of processing. In fact, from Table 3 one finds that V1 and V2 are quite different rheologically as a consequence of the ripening step, which introduces a different balance of electrostatic charges due to the variation of xanthate number per chain.

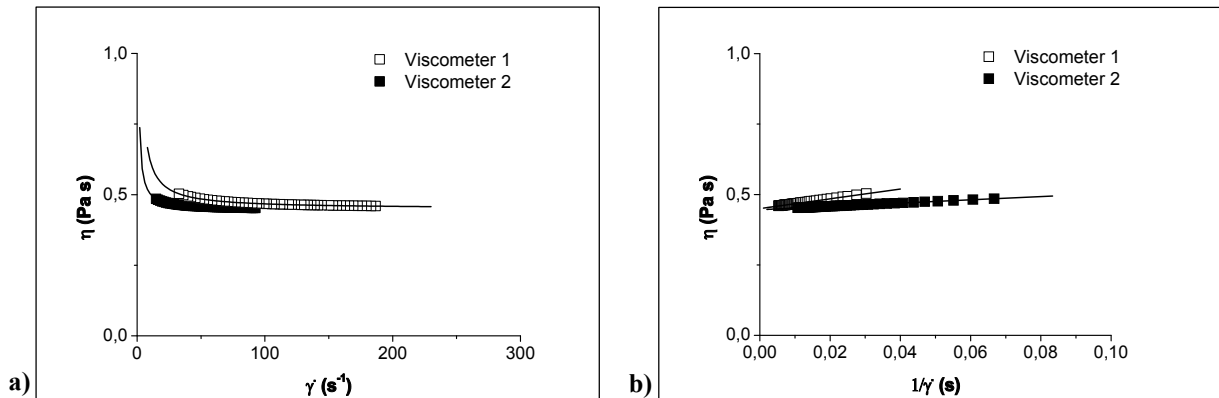


Figure 3. Shear viscosity as a function of shear rate for the reference viscose V2. Solid lines are fits of experimental data (symbols) with the Bingham model.

The reference viscose V2 was also studied in the Viscometer 2. Figure 3-a shows η versus $\dot{\gamma}$ for V2 by using both viscometers. Here the rheological parameters obtained from the lineal regression of the experimental data indicated in Fig. 3-b are $\tau_y=1.737$ Pa and $\eta_p = 0.450$ Pa s when Viscometer 1 was used, and $\tau_y = 0.583$ Pa and $\eta_p = 0.446$ Pa s with Viscometer 2. These results showed that a good reproduction of η_p values was obtained while the evaluation of τ_y associated with the slope of lines in Fig 3-b, became sensitive to the flow end effect at high draining times as a consequence of the smaller capillary radius used. Thus at high draining times the flow at the exit of the capillary was in the “dropping regime”, which perturbed the steady rheometric flow expected. This observation indicated that a further lowering of the shear rate was not possible for the capillary length used in the Viscometer 2.

CONCLUSIONS

From the correlation of rheological and basic physicochemical parameters of viscose formulations coded V1, V2 and V3, it was deduced that cellulose chains in the semi-concentrated solution regime presented a complex conformation involving high negative charge number with occluding hydration water. Thus, both the effective electrical charge and the average hydration of cellulose chains as a function of the DS and DP may be relevant parameters to be controlled for defining processing viscose solutions.

In particular, based on the reference viscose considered here, it was clear that the pulp combined pre-treatment used had a mild effect on the DP. On the other hand the ripening process introduced a significant effect on the reference viscose rheology evaluated through the plastic viscosity and yield stress.

Forthcoming works should focus on a deeper understanding of these microstructural electrokinetic phenomena on viscose solution rheology.

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